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Chemical Degradation of Siloxane Stress Cushions (M97 and S5370) by Thermal, Mechanical and Spectroscopic Investigations

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CHEMICAL DEGRADATION OF SILOXANE STRESS CUSHIONS (M97 AND S5370) BY THERMAL, MECHANICAL AND SPECTROSCOPIC INVESTIGATIONS

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Abstract

We are currently investigating the long term aging of weapon organics in an effort to develop predictive capabilities for functional service life. As part of this effort, we have been studying multimechanism aging of M97 and S5370 stress cushions. Ionizing radiation, thermal degradation, and desiccation all affect the crosslink density and motional dynamics and thus the engineering performance of these materials. Our approach has been to develop molecular level understanding of the effects of such aging mechanisms on polymer properties by a combined approach utilizing solvent swelling, thermal, DMA, molecular modeling, and solid state NMR. This presentation will offer a survey of our current work, concentrating on the application of solid state NMR for correlating structure and polymer dynamics. An overview of the relationships between crosslink density, NMR relaxation times, polymer chain dynamics, and storage modulus measurements will be presented and the advantages of NMR will be discussed. It will be shown that silicone based polymers tend to crosslink upon exposure to γ-radiation, undergo chain scission upon thermal degradation, and stiffen upon desiccation.

Introduction

Silica-filled polydimethylsiloxane (PDMS) composite systems are of broad appeal due to their chemical and environmental resilience and the availability of a wide range of tailorable chemical and mechanical properties [1-3]. M97 and S5370 type composites have been used for decades in weapon applications and the composite material is generally considered stable over long service lifetimes against numerous stress inducing aging mechanisms: thermal and mechanical loads, and environmental, radiative, and chemical attack. However, little data specific to these materials has been documented. In fact, the mechanical property changes associated with long term service in multi-mechanism degradating environments may be subtle and may not necessarily change linearly as a function of time in service. Since such linear relationships are often used in service lifetime predictions, there is a fundamental need to employ sensitive methods to investigate the structural and motional changes that occur in these materials as a result of aging in chemically, thermally, or radioactively harsh environments. Toward this end, we have employed a multitechnique investigation of chemical degradation effects on the dynamic and mechanical properties of both M97 and S5370 type cellular silicone

materials This presentation will offer a survey of our current work, concentrating on the application of solid state NMR for correlating structure and polymer dynamics.

Experimental

Materials

The chemical composition and synthesis schemes for M97XX and RTV5370 type cellular silicones are discussed elsewhere [4]. Radiation aged samples were irradiated in a stainless steel container (V ~ 2 liters) that was exposed to a Co^{60} source (1.2 MeV, 5 kGray/hr) for various periods of time. All experiments were performed at the same dose rate. Cumulative doses were determined by multiplying the exposure time by the dose rate (5 kGray/hr). Thermally aged samples were sealed in 5mm NMR tubes in a N2 atmosphere and aged in either a drying oven (T<100C) or a Thermolyne tube furnace (T>100C).

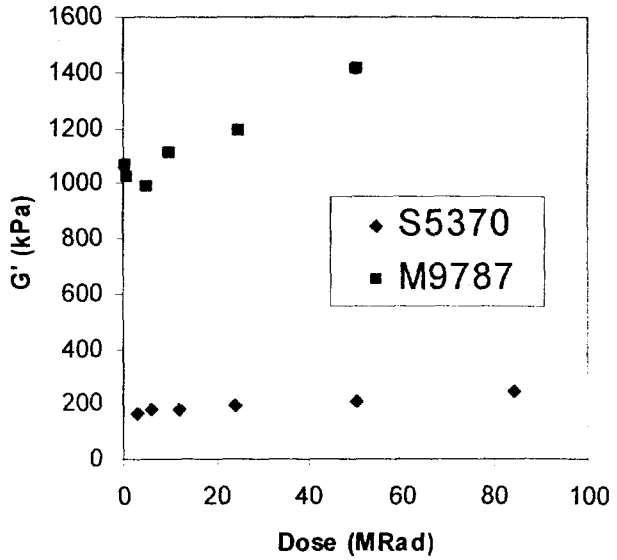

Figure 1. Storage Modulus versus cumulative dose of γ-radiation in air for M9787 and S5370 cushions.

DSC

DSC analyses were performed (TA Instruments, MDSC 2920, New Castle, DE) by cooling the sample at a rate of 6°C/min. to –150°C from room tem-perature. Heating of the samples was then performed at 3 °C/min. with a mod-ulation frequency of ~0.04°C/50 sec. Some DSC samples were analyzed with the addition of an isothermal dwell of up to 2 hours at –83°C on the cool down cycle prior to commencing the rest of the run.

DMA

DMA testing was performed (Rheometrics RMS-800 Dynamic Mechanical Spectrometer, Piscataway, NJ) in parallel plate geometry with a static compression force of 400g. Specimens were disks 1 mm in thickness and 13 mm in diameter. The sample

was sheared at a frequency of f=6.3 rad/sec. The maximum strain placed upon the sample was 0.5%.

NMR

NMR experiments were performed at 11.7 T on a Bruker DRX-500 NMR spectrometer and at 7.05 T on a Chemagnetics CMX-300 spectrometer. 1H transverse relaxation times (T_2) were measured by a spin-echo sequence. T2e values were obtained by measuring the time it took the echo intensity to reach 1/e of its starting value. Residual dipolar couplings were obtained via three methods: complete analysis of the time dependence of the echo decay, 2D multiple quantum methods, and dipolar correlation effect NMR methods. Details of these methods are discussed elsewhere [4, 5].

Molecular Modeling

Details of our molecular modeling approach are reported elsewhere [6].

Results and Discussion

DSC thermograms on irradiated M97 and S5370 materials show a change in the crystallization heat of fusion. With increasing cumulative dose, the heat of fusion was seen to decrease steadily. Kinetics of the crystallization phenomena have been studied by both DSC and DMA and show that the kinetics of crystallization have changed for both M97 and S5370 due to radiation induced crosslinking [7].

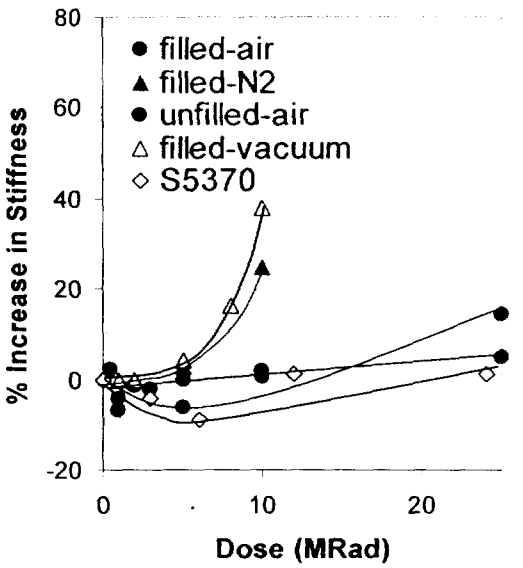

Figure 2. Results of NMR investigations of radiation damage to M9787 and S5370 cushions in a variety of atmospheres.

Results of DMA studies on γ-irradiated M97 and S5370 are shown in Figure 1 and show that as cumulative dose is increased, an observable change in polymer hardness

is detected. Previous solvent swelling results have shown that the increased stiffness of the polymer matrix is due to radiation induced crosslinking.

Results of spin-echo NMR studies of irradiated M97 and S5370 are shown in Figure 2 and show remarkable resemblance to the DMA results. Our indepth studies [4, 5] have shown that both the NMR and DMA response are related to the crosslink density changes occurring during irradiation. Our work has shown a linear dependence of $1/T_2$ on crosslink density over moderate changes. Since, from rubber elasticity theory [8] the storage modulus is also linearly dependent on the crosslink density, the agreement of the NMR and DMA results is not suprising.

We have employed this correlation to investigate aging signatures in situ for thermal degradation and desiccation. In these studies, small samples of polymer were sealed in NMR tubes and aged for various times. Without needing to remove the sample from the aging container, NMR results could then be acquired. Figure 3 shows the results of our initial thermal degradation studies performed at 100C for both M97 and S5370 materials. As can be seen, there is a slow decrease in $1/T_2$ for S5370 and M97. This suggests that thermally activated chain scissioning may be occurring at 100C.

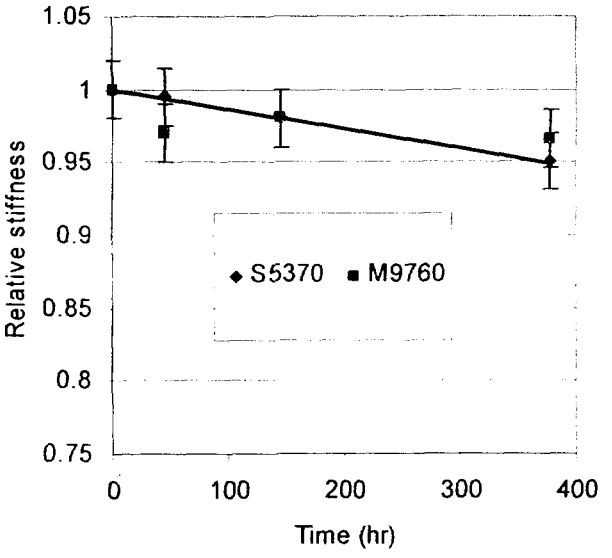

Figure 3. Change in relative stiffness as measured by NMR spectroscopy for M9760 and S5370 cushions as a function of time at 100 °C in a N_2 atmosphere.

Figure 4 shows the results of our in situ desiccation experiments. Samples of M97 were aged over P_2O_5, LiH, and molecular sieve for times exceeding 4 months. With increasing exposure to the desiccant, increasing stiffness occurs.

In an effort to validate our experimental observations, we have employed Molecular Dynamics simulations of the effect of water removal from a PDMS-silica interface [6]. The results are shown in Figure 4B and clearly show that as the silica surface is depopulated of hydroxyl species, the polymer interacting with the surface stiffens considerably.

Conclusions

We have studying the effects of numerous chemical aging mechanisms on the mechanical and dynamic properties of M9787 and S5370 silica filled PDMS based porous stress cushions. Radiation has been shown to induce chemical crosslinks that stiffen the polymer, slow polymer chain dynamics, and slow the kinetics of crystallization at –85C. Aging in N_2 atmospheres at 100°C causes chain scission after 10 days. Aging of M97 in a desiccating environment causes polymer chain stiffening as measured by NMR and predicted by MD calculations.

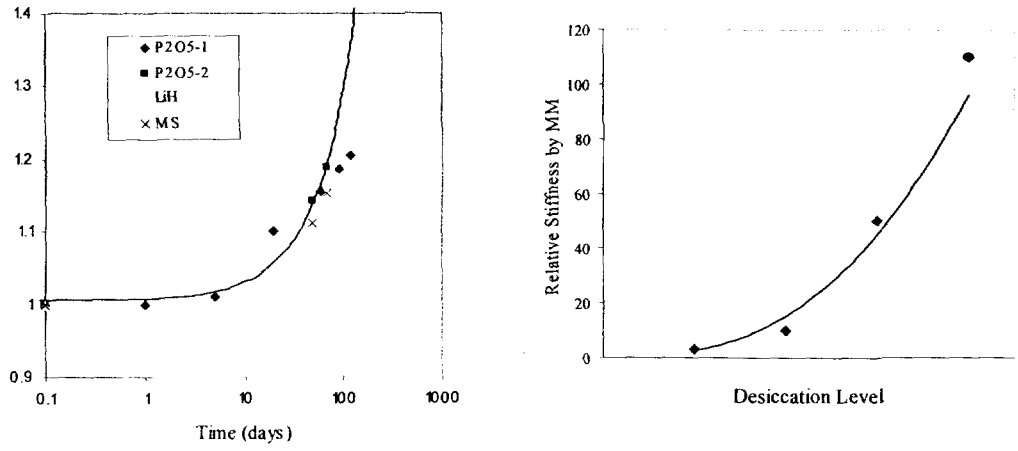

Figure 4. (A) Change in polymer stiffness with time exposed to various desiccants; (B) Change in relative stiffness as calculated from MD simulations as a function of surface hydration

Acknowledgments:

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References

1. J. M. Zeigher and F. W. G. Fearon, *Silicon Based Polymer Science: A Comprehensive Resource. Advances in Chemistry 224,* ACS Press (1990).
2. G. Kraus, Rubber Chem. Tech., **38** 1070 (1965)
3. P. Vondracek and A. Pouchelon, Rubber Chem. Technol., **63**, 202 (1990).
4. A. Chien, R. S. Maxwell, D. Chambers, B. Balazs, J. LeMay, J. Rad. Phys. Chem., **59** 493 (2000).
5. R. Maxwell and B. Balazs, J. Chem. Phys., in press (2002).
6. L. N. Dinh, M. Balooch, J. D. LeMay, J. Colloid. Inter. Sci. **230**, 432-440 (2000).
7. L. N. Dinh, M. A. Schildbach, M. A. McLean II, R. S. Maxwell, B. Balazs, J. D. LeMay, M. Balooch, *H_2O outgassing in and its effects on M9787 silicone*, UCRL-ID-145882.
8. Gee, et al, MRSS Proc, in press (2002).
9. A. Chien[1], S. Deteresa[2], R. Cohenour[3], J. Schneider[3] . Lemay[1], B.Balazs, *Crystallization Behaviour of M97 Cellular Silicones*, UCRL-ID-14036
10. J. Ferry, *Viscoelastic Properties of Polymers*, Wiley, NY (1980).